



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>C02F 3/30</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/07664</b>  <b>(43) International Publication Date:</b> 26 February 1998 (26.02.98)
<b>(21) International Application Number:</b> PCT/NL97/00482  <b>(22) International Filing Date:</b> 25 August 1997 (25.08.97)  <b>(30) Priority Data:</b> 1003860                      23 August 1996 (23.08.96)      NL 1005343                      21 February 1997 (21.02.97)      NL  <b>(71) Applicant (for all designated States except US):</b> TECHNISCHE UNIVERSITEIT DELFT [NL/NL]; Julianalaan 134, NL- 2628 BL Delft (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN LOOSDRECHT, Marinus, Cornelis, Maria [NL/NL]; Viool 99, NL-2678 HL De Lier (NL). JETTEN, Michaël, Silvester, Maria [NL/NL]; Schijfflaan 12, NL-2625 KG Delft (NL).  <b>(74) Agent:</b> ALTENBURG, Bernardus, Stephanus, Franciscus; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL- 1017 XS Amsterdam (NL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>
<b>(54) Title:</b> METHOD OF TREATING AMMONIA-COMPRISING WASTE WATER  <b>(57) Abstract</b>  <p>The invention relates to a method of treating ammonia-comprising waste water in which the bicarbonate ion is the counter ion of the ammonium ion present in the waste water. According to the invention half the ammonium is converted into nitrite, yielding an ammonia- and nitrite-containing solution, and in the second step the nitrite is used as oxidant for the ammonia. In the method according to the invention the conversion of half the ammonia into nitrite occurs automatically, providing a method which requires fewer controls. Also, the method according to the invention requires no external additive.</p>		

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## Method of treating ammonia-comprising waste water

The present invention relates to a method of treating ammonia-comprising waste water, wherein in a first step ammonia-comprising waste water is subjected to a nitrification treatment by using a nitrifying microorganism and by the addition of oxygen, yielding a solution comprising an oxidation product of ammonia, and in a second step the oxidation product of ammonia together with ammonia is converted into nitrogen, through the influence of a denitrifying microorganism.

Such a method is known from US patent specification No. 5,078,884. The nitrate formed by the oxidation of ammonia is used as an oxidant to convert, under substantially anaerobic conditions and with the aid of a microorganism, still to be degraded ammonia which acts as electron donor. During this process nitrogen is formed which is discharged into the atmosphere.

The disadvantage of this method is that there is no reliable degradation of ammonia, as can be seen in (the right half of) Fig. 2 of said publication. This means that undesirable discharges into the surface water may take place. To prevent this, all kinds of investments such as control and measuring equipment would be required. Finally, this method involves the addition of lye (see reaction equation 5 of said publication), which must also be controlled.

The objective of the present invention is to improve the method according to the preamble and in particular to provide a cost-effective, more reliable method which requires no additives and partly because of that, is simpler from a control-technological point of view.

Surprisingly, this objective can be achieved by a method which is characterized in that by using bicarbonate-containing waste water which is substantially stripped of bicarbonate by the supply of air, and in the first step maintaining the pH at  $\leq 7.2$  by controlling the aeration, part of the ammonia present in the waste water is con-

verted into nitrite, yielding a nitrite-containing solution, and in the second step the denitrifying microorganism uses the thus formed nitrite as oxidant for the remaining ammonia.

5 In this manner a method is provided offering considerable advantages, one of which being a substantially more self-regulatory nature. Moreover, the use of additives is avoided.

From the prior art a method is known, comprising a  
10 nitritification step in which ammonia is converted into nitrite. In a denitritification step the nitrite is converted into nitrogen while an organic carbon source is added as substrate for a denitritifying organism. As organic carbon source methanol is used. When said methanol  
15 is degraded, acid, formed during the nitritification step, is consumed, providing the pH control of the denitritification process. The disadvantage of this non-continuous method is that an additive is required and much control is required such as time control and substrate feed control.  
20 The total conversion of ammonia is not under all conditions satisfactory and is limited to at the most 90% and for this reason a subsequent treatment is often required.

A first favourable embodiment of the method is characterized in that in the first step the ammonia-containing  
25 ing waste water is fed to a nitritification reactor in an amount such that the nitritification reactor operates without sludge retention, the temperature of a solution subjected to nitritification is maintained at between 25 and 60°C and the pH at between 6 and 7.2.

30 In this manner favourable conditions are provided for the conversion of ammonia to nitrite, not nitrate.

In the second step, the temperature of the solution in the denitritification reactor being subjected to the denitritification treatment is preferably maintained at  
35 between 25 and 60°C and the pH at between 6 and 9.

In this manner favourable conditions are provided for the conversion of nitrite and ammonia into nitrogen.

According to a second embodiment of the method in accordance with the invention the first step and the sec-

ond step are carried out simultaneously in one bioreactor, in which bioreactor nitrifying and denitrifying microorganisms are present in a solid phase, the nitrifying microorganism being substantially present in the outer, aerobic part of the solid phase and the denitrifying microorganism being substantially present in the anaerobic inner part of the solid phase, and oxygen, dependent on the ammonia concentration in the bioreactor, is supplied in an amount limiting the first step.

10 The advantage of this method is that only one reactor is required. The preferably somewhat rough carrier comprises a biofilm, that is to say a layer comprising the nitrifying and denitrifying microorganisms, and the first step takes place in the outer, aerobic part of the bio-  
15 film. Because of oxygen limitation this outer, aerobic part of the biofilm is unable to convert more than 50% of the ammonia supplied and the ammonia, together with the nitrite formed in the outer, aerobic part of the biofilm, will be converted in the inner, aerobic part of the bio-  
20 film into nitrogen. The solid phase may consist of a spontaneously formed aggregate.

Preferably as solid phase a phase chosen from a biofilm-carrying particulate carrier and a biofilm-carrying immobile carrier is used.

25 If the carrier is particulate, the size of the carrier is preferably 0.1 to 1 mm. In this manner a high biomass density is provided and the size of the bioreactor can be kept to a limit. In a typical case the ammonia load of the biofilm surface is greater than 2-3 g N/m<sup>2</sup>·day.  
30 Some roughness of the carrier surface is an advantage.

In the second step the temperature of a solution subjected to the denitrification-nitrification reaction in the reactor is preferably maintained at between 5 and 60°C and the pH at between 6 and 9.

35 This creates favourable conditions for the conversion of ammonia into nitrogen.

The invention will be further elucidated by means of the detailed specification hereinbelow referring to an

Example of the method according to the invention, the parameters of which are given in the accompanying Figure.

The method according to the present invention comprises a nitritification reaction and a denitritification  
5 reaction. As can be seen from the overall-reaction equation I shown on the formula sheet, and as will be elucidated below, no addition of pH-adjusting means is necessary. The nitritification according to reaction equation II yields two equivalents of protons per converted equivalent  
10 ammonia. In waste water that can be suitably treated by applying the invention,  $\text{HCO}_3^-$  is the counter ion of the ammonia ion. Examples of such waste water include the percolation water from rubbish dumps and the effluent from aerobic purifications. The supply of air necessary for the  
15 oxidation of ammonia during the nitritification reaction, also ensures that  $\text{CO}_2$  is removed in accordance with reaction equation III. Accordingly, the nitritification reaction has a net yield of one equivalent acid per converted equivalent ammonia. The denitritification reaction according  
20 to reaction equation IV requires one equivalent acid per converted equivalent ammonia. This means that by using the  $\text{CO}_2$ -stripped effluent from the nitritification reactor, no pH adjustment is required.

By removing  $\text{CO}_2$ , the solution subjected to nitriti-  
25 fication is stripped of  $\text{HCO}_3^-$ , lowering the buffering capacity of the solution. This means that its pH may vary, in particular that it may drop due to the formation of acid in this step. The pK of  $\text{HCO}_3^-$ , that is to say the pH at which  $\text{HCO}_3^-$  buffers optimally, is 6.37. The drop of the pH  
30 inhibits the nitritification process, and ammonia is converted only partly but, according to the understanding provided by the present invention, to the desired extent (namely up to 50%). As a result, a suitable amount of ammonia is available for the subsequent denitritification  
35 process which uses acid and thus benefits from the low pH.

Without being bound to any theory, applicant assumes that the good controlling quality is achieved due to the fact that the nitritifying organism only perceives  $\text{NH}_3$  and  $\text{HNO}_2$  and not  $\text{NH}_4^+$  and  $\text{NO}_2^-$ . When the pH drops the

$\text{NH}_3$  (substrate) concentration decreases and the  $\text{HNO}_2$  concentration which inhibits the nitrification reaction, increases.

5           Example

          An agitated batch reactor (2.4 l) was operated without sludge retention and fed with ammonia-rich waste water (41 mM; pH ~ 8.0). During the day 80% of the reactor volume was replenished. The temperature was maintained at  
10 33°C and the dissolved oxygen concentration was 20%. Under these conditions the biomass concentration was 140 mg dry weight per litre. The pH of the reactor's effluent was about 6.7. N.B.: the pH was not adjusted by the addition of a substrate compound such as methanol. 40-50% of the  
15 ammonia in the waste water was converted.

          1.2 ml/min of the effluent was fed into a fluidized-bed reactor (capacity 2 l). The pH in the fluidized-bed reactor was stable and was about 7.9. Kjeldahl nitrogen was converted in the fluidized-bed reactor  
20 at a rate of 0.6 kg N/m<sup>3</sup>·day. The total removal of nitrogen was 83%. The relevant parameters are given in the Figure.

          This percentage may be increased by returning a portion of the effluent from the fluidized-bed reactor to  
25 the batch reactor. Due to the stable pH in the fluidized-bed reactor the amount of return is not very critical and may be set at a permanent value. Too high a return results in an increased degradation of ammonia in the batch reactor. This causes the consumption of acid to drop in the  
30 fluidized-bed reactor, as a consequence of which the degradation of ammonia decreases again.

          Although the method according to the invention has a substantially more self-regulatory nature and automatically results in an overall degradation of ammonia of at  
35 least about 80%, the pH of the contents of the nitrification reactor may optionally be adjusted by means of the supply of effluent from the denitrification reactor. Thus here no external additive whatsoever is added.

According to another embodiment of the method according to the invention, the waste water is fed to a denitritification step. During denitritification ammonia from the waste stream is used and a portion from the denitritification reactor is fed to the nitritification reactor. There nitrite is formed which is fed to the denitritification reactor.

In the event that the effluent from the denitritification step is discharged, said effluent may first be subjected to a nitrification step in order to avoid nitrite discharge.

Suitable microorganisms may be obtained without great difficulty from sludge of existing water-treatment plants in which ammonia is degraded, in the manner described in the literature. Alternatively, the culture for the denitritification may be obtained from the Centraal Bureau voor Schimmelcultures, Baarn, the Netherlands, registered under number 949.87.



CLAIMS

1. A method of treating ammonia-comprising waste  
5 water, wherein in a first step ammonia-comprising waste  
water is subjected to a nitrification treatment by using a  
nitrifying microorganism and by the addition of oxygen,  
yielding a solution comprising an oxidation product of  
ammonia, and in a second step the oxidation product of  
10 ammonia together with ammonia is converted into nitrogen,  
through the influence of a denitrifying microorganism,  
characterized in that by using bicarbonate-containing  
waste water which is substantially stripped of bicarbonate  
by the supply of air, and in the first step maintaining  
15 the pH at  $\leq 7.2$  by controlling the aeration, part of the  
ammonia present in the waste water is converted into  
nitrite, yielding a nitrite-containing solution, and in  
the second step the denitrifying microorganism uses the  
thus formed nitrite as oxidant for the remaining ammonia.

20 2. A method according to claim 1, characterized in  
that in the first step the ammonia-containing waste water  
is fed to a nitritification reactor in an amount such that  
the nitritification reactor operates without sludge reten-  
tion, the temperature of a solution subjected to nitriti-  
25 fication is maintained at between 25 and 60°C and the pH  
at between 6 and 7.2.

3. A method according to claim 1 or 2, character-  
ized in that in the second step, the temperature of the  
solution in the denitritification reactor being subjected  
30 to the denitritification treatment is preferably main-  
tained at between 25 and 60°C and the pH at between 6 and  
9.

4. A method according to claim 1, characterized in  
that the first step and the second step are carried out  
35 simultaneously in one bioreactor, in which bioreactor  
nitrifying and denitrifying microorganisms are present in  
a solid phase, the nitrifying microorganism being substan-  
tially present in the outer, aerobic part of the solid  
phase and the denitrifying microorganism being substan-

tially present in the anaerobic inner part of the solid phase, and oxygen, dependent on the ammonia concentration in the bioreactor, is supplied in an amount limiting the first step.

5           5. A method according to claim 4, characterized in that as solid phase a phase chosen from a biofilm-carrying particulate carrier and a biofilm-carrying immobile carrier is used.

10           6. A method according to claim 1 or 2, characterized in that the temperature of a solution in the reactor being subjected to a denitrification-nitrification treatment is maintained at between 5 and 60°C and the pH at between 6 and 9.

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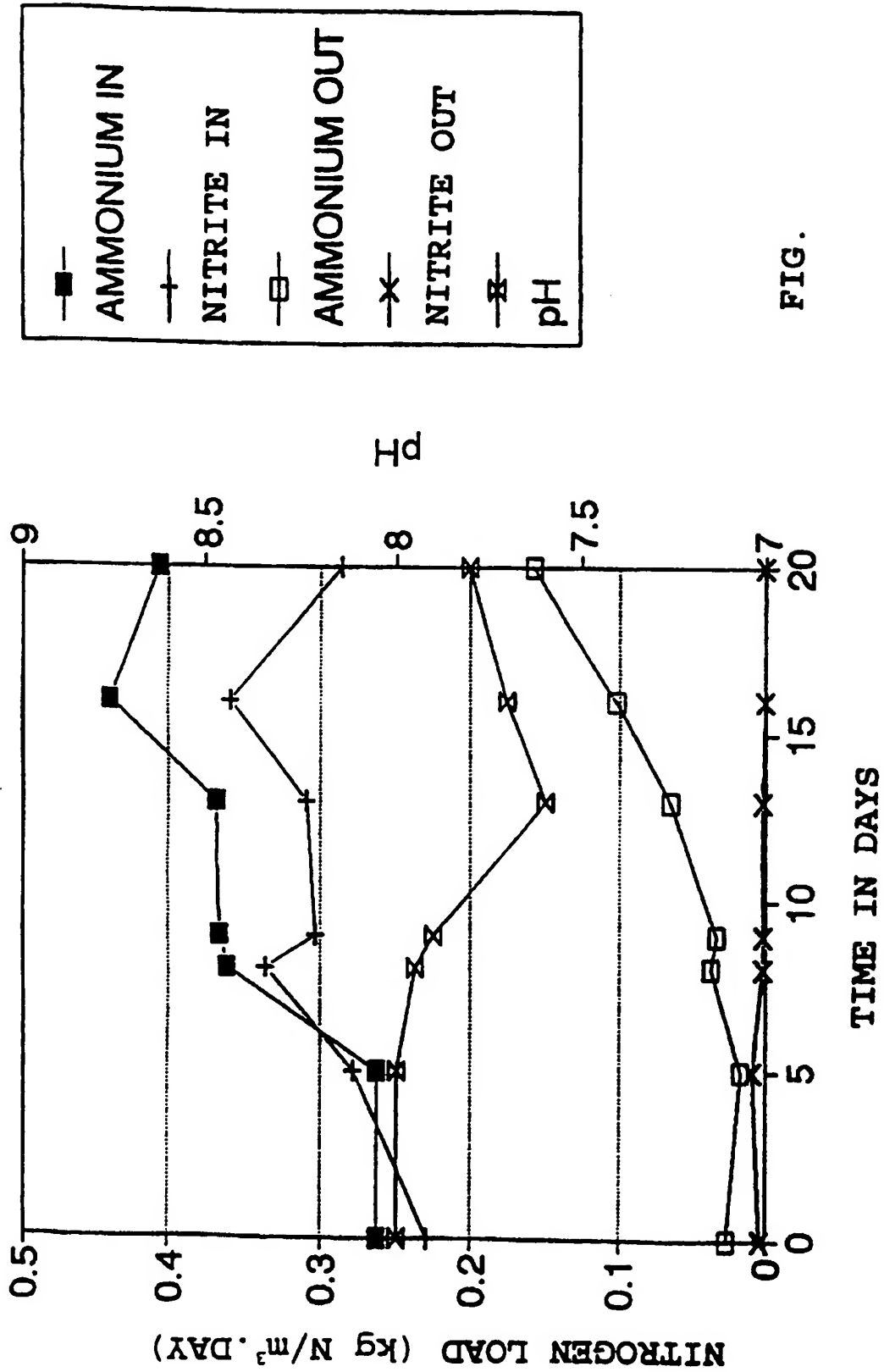
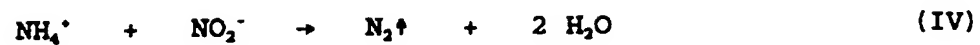
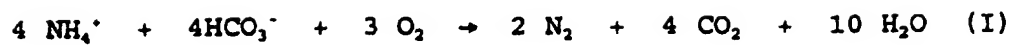


FIG.

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FORMULA SHEET

## INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/NL 97/00482

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C02F3/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ARNO SCHRAUWERS: "Eenreactor stistofverwijderingsproces paart eenvoud aan schoonheid" DELFT INTEGRAAL, vol. 12, no. 1, 1995, DELFT-NL, pages 3-7, XP002030429 ---	1-3
A	DE 39 39 732 A (PREUSSAG AG) 6 June 1991 -----	1



Further documents are listed in the continuation of box C.



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Date of the actual completion of the international search

17 November 1997

Date of mailing of the international search report

26 11. 97

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00482

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DE 3939732 A	06-06-91	NONE	